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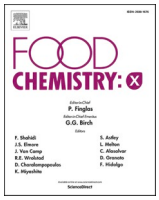

Miniaturized solid-phase microextraction coupled with gas chromatography-mass spectrometry for determination of endocrine disruptors in drinking water

Mereke Alimzhanova [a,b,*], Madina Mamedova [a,b], Kazhybek Ashimuly [b], Alham Alipuly [b], Yerlan Adilbekov [b]

[a] al-Farabi Kazakh National University, Faculty of Physics and Technology, 71 al-Farabi Ave., 050040 Almaty, Kazakhstan
[b] Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, 050012 Almaty, Kazakhstan

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ABSTRACT

A simple and rapid method based on miniaturized solid-phase microextraction (mini-SPME) followed by gas chromatography–mass spectrometry was developed to identify eight endocrine disruptors (atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinylestradiol, norgestrel, and megestrel) in drinking water samples. Extraction parameters was optimized and further analyses was performed using them. The optimum temperature for the determination of endocrine disruptors in water was 80 °C; the optimum extraction and preincubation times were 60 and 20 min, respectively. The studied linear range of endocrine disruptors was 10.0–1000 μg mL^{-1}. The limit of detection ranged from 0.020 to 0.087 μg mL^{-1}. The correlation coefficient (r^2) was 0.96–0.99. This research introduces a novel method for detecting analytes at extremely low concentrations, as well as the possibility of combining several detection technologies to give high-accuracy qualitative and quantitative determination of endocrine disruptors in aqueous samples.

Introduction

The most important component of public health is the quality of drinking water, as poor-quality drinking water can affect many aspects of human existence. The absence of contaminants in drinking water is the most important criteria for ensuring its safety. According to (Wee et al., 2021), contamination of drinking water with endocrine-disrupting compounds (EDCs) is a growing problem globally.

The presence of endocrine disruptors in water may be due to contamination of spring water, contamination during production and bottling, or migration of substances from the packaging. Possible sources of contamination include unintentionally introduced substances because of the technological process. These are contamination and decomposition products from closures, sealing materials for them, pipe materials, pump systems, storage containers, cleaning and disinfecting agents. A significant group of pollutants are pesticides, humic substances and phthalates (Gonsioroski et al., 2020).

The Endocrine Society defines endocrine disruptors as "exogenous (unnatural) chemicals or mixtures of chemicals that interfere with any hormone action". Hormones, in turn, are biologically active substances of organic nature that are produced in specialized cells of the endocrine glands that enter the blood, bind to the receptors of target cells, and have regulatory effects on metabolism and physiological functions (Gore et al., 2014).

EDCs are chemicals that disrupt the endocrine system, interacting with it as endogenous hormones. EDCs block hormone receptors and can ultimately disrupt physical development (Münze et al., 2017). Infertility, thyroid dysfunction, infection susceptibility, autoimmune illness, and heart disease have all been linked to high levels of EDCs in humans (Köck-Schulmeyer et al., 2013).

Currently, more than 200 substances are known that have a detrimental effect on the endocrine system. Among them are hormones (diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, and megestrel), parabens, pesticides (atrazine), and phthalates (bisphenol A). These substances are found in many everyday objects and can easily enter our body (De Coster & Van Larebeke, 2012). Sanfilippo et al. (2010) identified trace endocrine disruptors, hormones (17-estradiol (E2), diethylstilbestrol (DES), 4-hydroxytamoxifen), phenolic

* Corresponding author.
E-mail address: alimzhanova.mereke@gmail.com (M. Alimzhanova).

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compounds, and phthalates (bisphenol A (BPA), di (2-ethylhexyl) phthalate (DEHP), 4-octylphenol (OF), and 4- *n*-nonylphenol (4-*n*-NF)) in ultrapure water samples for laboratory use by gas chromatography-mass spectrometry (GC–MS). Carles et al. (2021) studied and compared the effect of atrazine and nitrates on fetal growth and development; however, they found no evidence that atrazine-contaminated water had a negative impact on prenatal development. However, the results of other studies (Almberg et al., 2018; Chevrier et al., 2011) suggested that exposure to EDC-contaminated water led to the birth of small for gestational age (SGA) or low birth weight (LBW) babies.

Other researchers (Hugo et al., 2009; Ying, 2012) reported that EDCs pose the highest risk for women during pregnancy or for fetuses during their early development, when organs and the nervous system are just beginning to form, leading to the possibility of preterm delivery. One of the most serious examples of this is diethylstilbestrol (DES), a synthetic estrogen drug (Thomas Zoeller et al., 2012). DES has been associated with a variety of side effects in women exposed during pregnancy and their fetuses. Endocrine diseases due to DES can manifest decades later and not only in the first, but also in the second and third generations (Petrovic et al., 2002).

The problem of developing methodological approaches for identifying endocrine disruptors in drinking water samples is of relevance. Analysis of the existing methodological base for the determination of endocrine disruptors in water samples showed that solid-phase microextraction coupled with chromatographic analysis was taken as the basis (Gibson et al., 2010; Tan et al., 2008).

Various researchers have identified endocrine disruptors using various solid-phase microextraction (SPME) methods. Bisphenol A was identified in drinking water by solid-phase extraction (SPE) and ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) (Moid AlAmmari et al., 2020). Steroids (estrone, estradiol and diethylstilbestrol) in water were analyzed by direct immersion SPME-GC-MS-MS (Chopra et al., 2014). Nonylphenol and octylphenol in water were determined using SPME and comprehensive two-dimensional gas chromatography with a flame ionization detector (Moreira et al., 2015).

These techniques enable the identification of selected analytes in extremely low concentrations, and the combination of various detection methods enables both the high-accuracy qualitative and quantitative determination of endocrine disruptors in aqueous samples (Magi et al., 2010).

The current study aimed to identify endocrine disruptors in drinking water samples using for the first time miniaturized solid-phase microextraction (mini-SPME) in combination with gas chromatography mass spectrometry method. The advantage of gas chromatography is its ability to effectively separate many components of the analyzed mixture. The use of mass spectrometry detection substantially expands the spectrum of compounds that can be determined by gas chromatography (Díaz-Cruz et al., 2003).

Compared with the SPME method, in our proposed mini-SPME method, 2 mL vials are used, and only a small amount of the target analyte, 1 mL, is required. When using the mini-SPME method, the time to reach equilibrium between the liquid phase and the fiber is considerably shorter, which increases the total analysis quality. This method will be useful for the efficient, rapid and inexpensive determination of endocrine disruptors in drinking water samples. With this proposed sample preparation method, toxic organic solvents are not required, making it a green method of analysis.

Materials and methods

Reagents and samples

EDC standards atrazine, diethylstilbestrol, estradiol, ethinylestradiol, norgestrel, hexestrol, estrone, megestrel was used in this study (Meryer, China). Distilled water obtained by electric bidistiller BE-4 (Livam, Russia). Helium gas, (>99.995%) in 40 L bottles, max. pressure 150 bar (Orenburg, Russia).

The process of choosing the optimal parameters of mini-solid phase microextraction for extracting analytes from water was carried out on real samples of drinking water.

Sample preparation

We added standard of an endocrine disruptor (atrazine, diethylstilbestrol, estradiol, ethinylestradiol, norgestrel, hexestrol, estrone, or megestrel) each weighing 0.01 g in a 20 mL vial. 10 mL of methanol is added to the vial with a pipette to obtain an initial solution with a concentration of 1000 mg mL^{-1}. Then, we shook and placed it in an ultrasonic bath to ensure the complete dissolution of substances. Calibration solutions are prepared from the stock solution (C = 1000 mg mL^{-1}).

In volumetric flasks, with a volume of 5 mL, 50, 250, 1250, 2500 μL we added from the stock solution (to obtain calibration solutions with concentrations of 10, 50, 250 and 500 μg mL^{-1}, respectively), and brought to the mark with methanol.

The methanol has been evaporated off for mini solid-phase microextraction analysis. From each calibration solution 0,1 mL was taken to 2 mL vials. Then the the methanol was at room temperature. Each calibration solution was prepared in four parallel steps. After evaporation, 1 mL of water was added, set in an ultrasonic bath for mixing and transfer of analytes to the aqueous phase.

Equipment

The extraction coating was injected using a MultiPurpose Sampler (Gerstel, Germany) into the sample injection device of a gas chromatograph with a 7890A/5975C mass spectrometric detector in splitless mode. Chromatography was performed using a DB-35MS capillary column with a length of 30 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 μm. The carrier gas (helium, grade "A") was supplied at a constant rate of 1.0 mL min^{-1}.

Desorption of analytes was carried out at a temperature of 270 °C for 20 min. The temperature of the column thermostat was programmed from 80 °C (exposure 1 min) to 200 °C (exposure 5 min) with a heating rate of 30 °C min^{-1}, and up to 300 °C (exposure 5 min) with a heating rate of 5 °C min^{-1}. The analysis time is 35 min. The MSD interface temperature was 320 °C, the temperature of the quadrupole was 180 °C, and the ion source temperature was 230 °C. Detected in the ion-scanning mode in the range of mass numbers *m/z* 50–950 a.m.u.

Agilent MSD ChemStation software (version 1701EA) was used to control the gas chromatograph system and the system for recording and processing chromatographic data. The data processing included the determination of the retention times of the test substance, the heights and areas of the peaks, as well as the processing of the spectral information obtained using the mass spectrometric detector. To decode the obtained mass spectra, the Wiley 11th edition and NIST'02 libraries were used.

Results and discussion

Optimization of extraction paramaters

Design of the experiments was based on the SPME protocol developed by Pawliszyn (Pawliszyn, 2012; Risticevic et al., 2010). Selection of fiber coating, extraction time and temperature, preincubation and desorption time are all main factors in optimizing SPME conditions for different samples. In water analysis, the extraction process determines a lot of the key parameters, such sensitivity, repeatability, reproducibility, precision and accuracy, limits of detection, quantification, and linearity (Abdulra'uf & Tan, 2015).

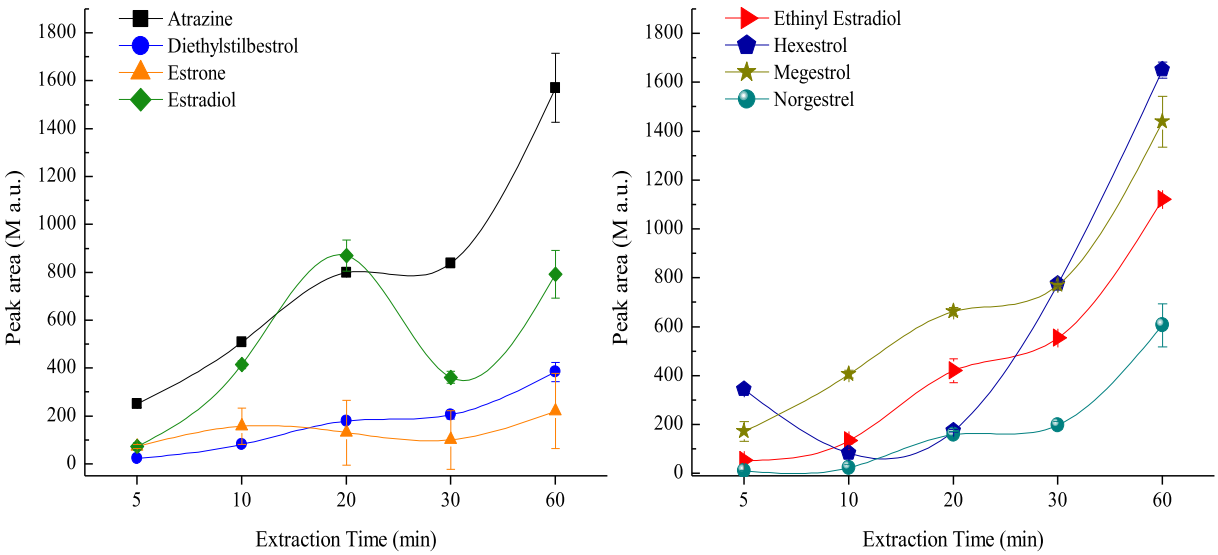

Fig. 1. The extraction time of atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, megestrel at 5, 10, 20, 30 and 60 min.

Selection of the optimal extraction time

The choice of the optimal extraction time is one of the important factor in achieving the maximum efficiency of the extraction of the studied components from the sample (Cháfer-Pericás et al., 2007; Mousa et al., 2013; Pawliszyn, 2012). The extraction time is set in accordance with the saturation of the analyzed compounds on the extraction coating of the fiber sufficient for identification by the mini-SPME GC–MS method.

During the optimization, the following extraction times were applied: 5; 10; 20; 30 and 60 min. Extraction temperature was 80 °C. Incubation and desorption times were set as both at 20 min. Initial temperature of the GC oven was set at 80 °C, exposure time at the initial temperature was 1 min. Followed by heating up to temperature 200 °C at the rate of 30 °C min^{-1}, exposure time at the final temperature 300 °C at the rate of 5 °C min^{-1}. Results of analysis of EDCs at different extraction times are presented in Fig. 1.

For the determination three EDCs and five endocrine steroid hormones by direct immersion solid-phase microextraction in aqueous and biological environmental samples were optimized (Yang et al., 2006). The extraction time was set at 120 min, the incubation temperature was 45 °C. With an increase in the extraction time to 120 min, the reactions of all target compounds increased and reached a near-equilibrium state.

The trace endocrine disrupting chemicals using multiple monolithic fiber solid-phase microextraction (MMF-SPME) utilizing polymeric ionic liquid-based adsorbent were studied (Pei et al., 2017). Also here, an increase in the extraction time shows an increase in the peaks of the target analytes. Hence, an optimal extraction time of 50 min was chosen here.

Therefore, in this study as seen on Fig. 1, an increase of extraction time from 5 to 60 min leads to an increasing of response by approximately 10 times of endocrine disruptors. However, an increase in extraction time will lead to an unstable analytical signal for estradiol, the highest peak of which is reached at 20 min, but the result shows that there is no large peak difference between 20 and 60 min. Thus, based on the data it was concluded that the 60 min is the optimal time of extraction, as it provides adequate detection of endocrine disruptors.

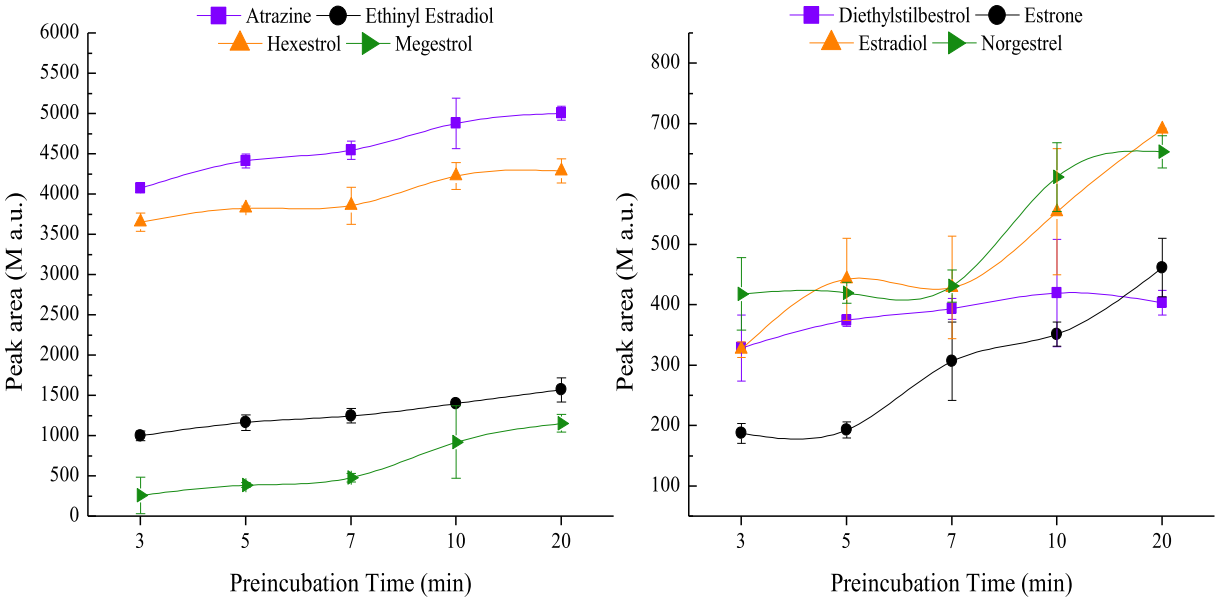

Fig. 2. The preincubation time of atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, megestrel at 3, 5, 7, 10 and 20 min.

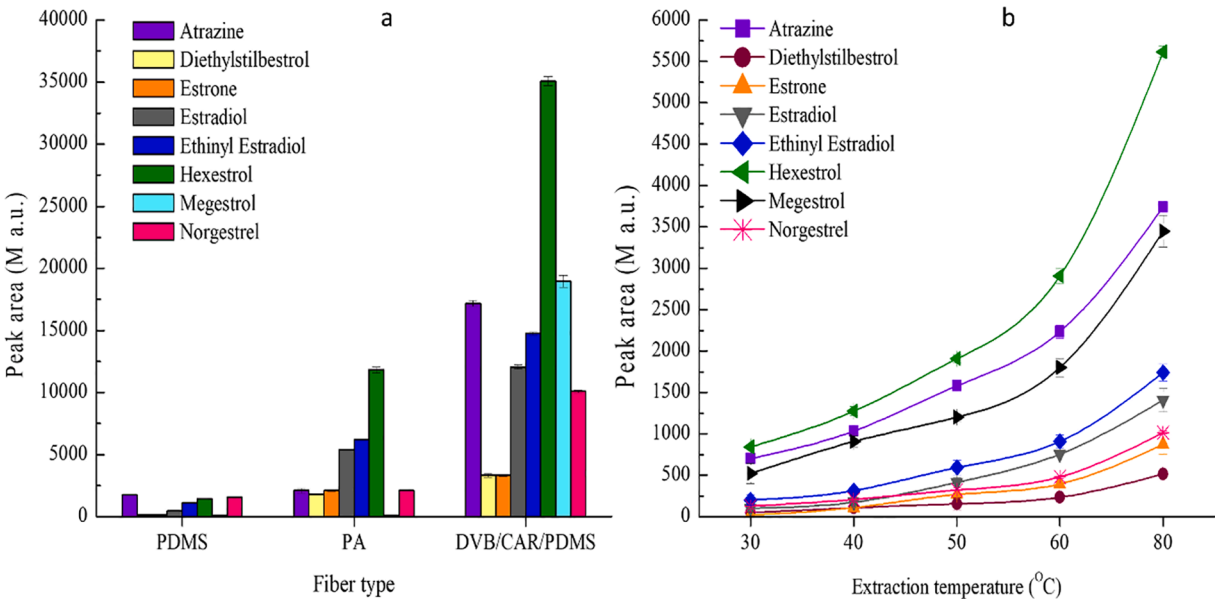

Fig. 3. (a) The comparison of fibers PDMS, PA, DVB/CAR/PDMS; (b) The comparison of extraction temperatures at 30℃, 40℃, 50℃, 60 and 80℃.

Selection of the optimal preincubation time

The preincubation time is necessary for the sample to reach the required extraction temperature, as well as to establish equilibrium between the gas and liquid phases during headspace-solid phase microextraction (Pawliszyn, 2012; Risticevic et al., 2010), whereas in the direct immersion-solid phase microextraction (DI-SPME) equilibrium takes place between fiber and sample matrix (Zhang et al., 2018), which is the same for the mini-SPME. The preincubation time has a significant effect on the process of solid-phase microextraction of organic compounds 3, 5, 7, 10, 20, and 30 min were tested to determine the optimal preincubation time for EDCs from drinking water samples (Fig. 2).

As shown by the results of the experiments, an increase in the pre-incubation time has a less effect on the extraction of EDCs, except for atrazine and hexestrol. The pre-incubation time of 20 min allows achieving the required equilibrium and sensitivity in the analysis of EDCs, so further analyzes are effective to perform at 20 min.

Selection of the optimal fiber type and temperature

Extraction coating is one of the most important parameters of solid phase microextraction. The composition and thickness of the extraction coating have a significant effect on the selectivity of mini-solid-phase microextraction of organic compounds from samples and the sensitivity of the method. The following extraction coatings were tested to determine the target analytes content in drinking water samples:

- 100 μm polydimethylsiloxane (PDMS);
- 50/30 μ divinylbenzene/carboxen/polydimethylsiloxane
- (DVB/CAR/PDMS);
- 85 μm polyacrylate (PA).

As a result, it was found that the greatest response EDCs provides an extraction coating based on 50/30 μm DVB/CAR/PDMS. This may be due to its multicomponent composition, which allows the extraction of a wider range of analytes (Fig. 3a).

The research (Risticevic et al., 2010) showed the PDMS and PA is an adsorption fibers that allows the main extraction of volatile and polar semi-volatile compounds with molecular weights from 30 to 225 and 80 to 300 respectively. Since these target analytes are compounds with

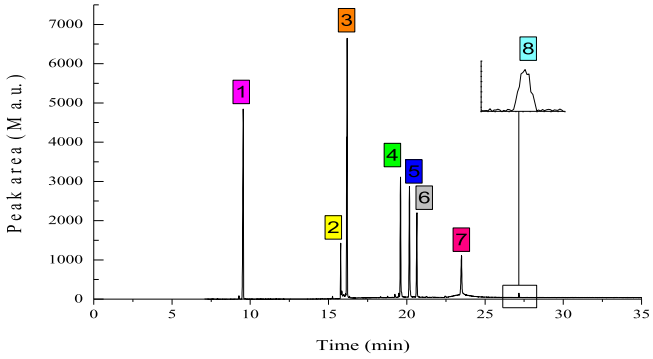

Fig. 4. Chromatogram of 1-atrazine, 2-diethylstilbestrol, 3-hexestrol, 4-estrone, 5-estradiol, 6-ethinyl estradiol, 7- norgestrel, 8-megestrel in drinking water samples.

rather high molecular weights 215–312 g mol^{-1}, as it is seen from the Fig. 3a fibers based on PDMS and PA do not provide the recovery of such compounds.

Optimization of temperature was carried out on drinking water samples contaminated with standards of endocrine disruptors. The extractive coating was exposed in a sample and held for 60 min at temperatures of 30℃, 40℃, 50℃, 60 and 80℃ temperatures (Fig. 3b).

The experimental results, presented in the form of a graph of the dependence of the peak area of analytes on the extraction temperature, showed that with an increase in the temperature from 30 to 80 °C, the degree of extraction of the analytes under study increases. Mousa et al. (2013) endocrine disruptors have a high boiling point of 154–200 °C therefore, temperatures significantly higher are required for the extraction from the drinking water samples. A temperature of 80 °C for endocrine disruptors provides maximum response and increases their concentration by 10 times. Thus, the optimal extraction temperature providing the greatest response to endocrine disruptors is 80 °C. It is not recommended to increase the extraction temperature above 80 °C, as high pressure is formed in the vial, which can cause the vial to crack or explode.

A simple and rapid method based on miniaturized solid-phase microextraction (mini SPME) technique followed by gas chromatography-mass spectrometry (GC–MS) was developed by the

Table 1
Analytical parameters of the proposed method.

Analytes	Linear range	r^2	LOD
Atrazine	10–1000	0.9992	0,020
Diethylstilbestrol	10–1000	0.9791	0,037
Hexestrol	10–1000	0.9976	0,024
Estrone	10–1000	0.9619	0,027
Estradiol	10–1000	0.9841	0,025
Ethinyl Estradiol	10–1000	0.9785	0,025
Norgestrel	10–1000	0.9757	0,053
Megestrel	10–1000	0.9612	0,087

simultaneous determination of 8 endocrine disruptors in drinking water Fig. 4. The mass concentrations of atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, megestrel in water were determined by gas chromatography with mass spectrometric detection in combination with mini-solid-phase microextraction in the concentration range of endocrine disruptors from 10 to 1000 μg mL^{-1}. The limit of detection was found in the range of 0.020–0.087 μg mL^{-1}. The correlation coefficient was found in the range 0.96–0.99 (r^2) (Table 1).

The available classical methods (Martínez et al., 2013; Selvaraj et al., 2014; Serrano et al., 2019; Zhao et al., 2009) for the determination of endocrine disruptors make it possible to obtain similar results. However, the miniaturized SPME-based technique significantly surpasses the known methods of their determination in terms of environmental friendliness and requires minimal sample amount, which makes the experiments cost efficient. Thus, miniaturized-SPME method allows the use of a very small amount of the target component, up to ten times less than in other studies (Yang et al., 2006), which makes it a suitable method for determination of other samples (e.g. food, beverages).

Conclusions

The results of the study showed that the miniaturized-SPME (mini-SPME) coupled with gas chromatography-mass spectrometry makes it possible to determine endocrine disruptors in drinking water samples.

During the optimization, it was concluded that fiber based on DVB/CAR/PDMS is the best option for the recovery of target analytes. Moreover, with an increase in the extraction temperature to 80 °C, the response of the peak of endocrine disruptors increased ten times, however it is not recommended to exceed this temperature. The pre-incubation time is necessary for the sample to reach the required extraction temperature, as well as to establish equilibrium between the gas and liquid phases. So the optimum pre-incubation time was established at 20 min and extraction time of 60 min. Linear range of endocrine disruptors from 10 to 1000 μg mL^{-1}. The limit of detection was found in the range of 0.020–0.087 μg mL^{-1}. The correlation coefficient was found in the range 0.96–0.99 (r^2).

CRediT authorship contribution statement

Mereke Alimzhanova: Supervision, Conceptualization, Funding acquisition, Data curation, Writing – original draft, Writing – review & editing. **Madina Mamedova:** Writing – original draft, Investigation, Validation, Software, Writing – review & editing. **Kazhybek Ashimuly:** Supervision, Formal analysis, Investigation, Visualization, Methodology, Writing – review & editing. **Alham Alipuly:** Visualization, Investigation, Methodology, Formal analysis. **Yerlan Adilbekov:** Formal analysis, Writing – original draft, Visualization, Validation, Data curation, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mereke Alimzhanova reports financial support was provided by Ministry of Education and Science of the Republic of Kazakhstan. There are no conflict of interests.

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Conflict of interests

Authors declare no conflict of interests.

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